

# Doping Dependence of Polaron Hopping Energies in $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ ( $0 \leq x \leq 0.15$ )

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Measurements of the low-frequency ( $f \leq 100$  kHz) permittivity at  $T \lesssim 160$  K and dc resistivity ( $T \lesssim 430$  K) are reported for  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$  ( $0 \leq x \leq 0.15$ ). Static dielectric constants are determined from the low- $T$  limiting behavior of the permittivity. The estimated polarizability for bound holes  $\sim 10^{-22} \text{ cm}^3$  implies a radius comparable to the interatomic spacing, consistent with the small polaron picture established from prior transport studies near room temperature and above on nearby compositions. Relaxation peaks in the dielectric loss associated with charge-carrier hopping yield activation energies in good agreement with low- $T$  hopping energies determined from variable-range hopping fits of the dc resistivity. The doping dependence of these energies suggests that the orthorhombic, canted antiferromagnetic ground state tends toward an insulator-metal transition that is not realized due to the formation of the ferromagnetic insulating state near  $\text{Mn}^{4+}$  concentration  $\approx 0.13$ .

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## I. INTRODUCTION

The  $\text{Mn}^{3+}$ -rich insulating compounds,  $\text{La}_{1-x}\text{A}_x\text{MnO}_3$  ( $\text{A}=\text{Sr}, \text{Ca}$ ,  $x \leq 0.15$ ) have attracted considerable interest in recent years for their inhomogeneous magnetic ground states,<sup>1</sup> and complex structural phase diagrams,<sup>2,3</sup> believed to be consequences of competing magnetic, lattice, and Coulomb interactions.<sup>4</sup> With regard to transport properties, there is general consensus that the charge-carriers in the high- $T$  paramagnetic phases of these compounds are small polarons.<sup>5,6,7</sup> However, few systematic studies of the doping dependence of polaron transport in the insulating regime have been reported.<sup>8</sup> The experimental situation is complicated by the sensitivity of the structural and magnetic properties to deviations in stoichiometry<sup>2,3</sup> and the uncertain stoichiometry of specimens employed in many early transport studies.

Here we present dielectric and dc resistivity measurements on a series of  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$  polycrystalline specimens with  $x \leq 0.15$  that offer new insight into the role of electron correlations on the changes in ground state magnetic and crystal structure that occur<sup>1,2,3</sup> near  $\text{Mn}^{4+}$  content,  $p = p_c \simeq 0.13$ . Consistent with the small-polaron picture, the doping dependence of the dielectric constant yields a bound-polaron polarizability that implies a localization length comparable to a lattice spacing. In agreement with prior work<sup>8</sup> on  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$  we find that the high-temperature polaron hopping energy is independent of  $p$  up to  $p_c$ , above which it begins to decrease. Particularly interesting are low-temperature measurements of dielectric relaxation and dc resistivity which indicate a polaron hopping energy that tends toward zero near  $p_c$ . These results suggest that charge-carriers within the orthorhombic, canted antiferromagnetic (CAF) phase are approaching an insulator-metal transition that is not achieved due to the emergence of the monoclinic and ferromagnetic insulating (FMI) phase.

## II. EXPERIMENT

Polycrystalline specimens of  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_{3+\delta}$  were prepared by standard solid-state reaction under Ar atmosphere; the preparation methods, structural characterization and magnetic properties are reported elsewhere.<sup>9</sup> Powder x-ray diffraction revealed no secondary phases; the average  $\text{Mn}^{4+}$  (hole) concentration ( $p = x + 2\delta$ ) was determined by iodometric titration (see Table I). A small and nearly  $x$ -independent oxygen excess ( $\delta_{av} \approx 0.017$ ) in the present specimens is attributed to cation vacancies<sup>10,11</sup> which contribute additional holes uniformly,<sup>11</sup> similar to Ca substitution. The structural and magnetic properties of the present specimens are consistent with those of stoichiometric compounds.<sup>3,11</sup>

AC impedance measurements were conducted with an HP4263B LCR meter at frequencies  $f = 100$  Hz, 120 Hz, 10 kHz, 20 kHz, 100 kHz using a 4-terminal pair arrangement. Reliable measurements of  $\varepsilon$  were restricted to  $T \lesssim 160$  K where the capacitive reactance was sufficiently large ( $\gtrsim 0.1\Omega$ ). Typical specimen dimensions were  $3 \times 1.0 \times 0.5 \text{ mm}^3$ . Silver paint electrodes were applied on the largest, polished faces of the specimens. Contact capacitance can lead to apparently large values<sup>12</sup> of  $\varepsilon$  and thus some care is required to distinguish the true response of the sample. To rule out the influence of contacts, the impedances of several specimens were re-measured after further polishing to reduce the electrode spacing by at least a factor of two; in all cases the low-temperature data used to determine  $\varepsilon_0$  agreed within geometric uncertainties of  $\pm 10\%$ . The results were also independent of applied ac voltage in the range 50mV-1V. At higher temperatures where dielectric relaxation was observed, some dependence on the electrode spacing was evident, consistent with a contribution from contact capacitance. This issue is addressed further below. Four-probe dc resistivity measurements were performed in separate experiments in air (high- $T$ ) and vacuum (low- $T$ ) with current applied along the long axis of the same

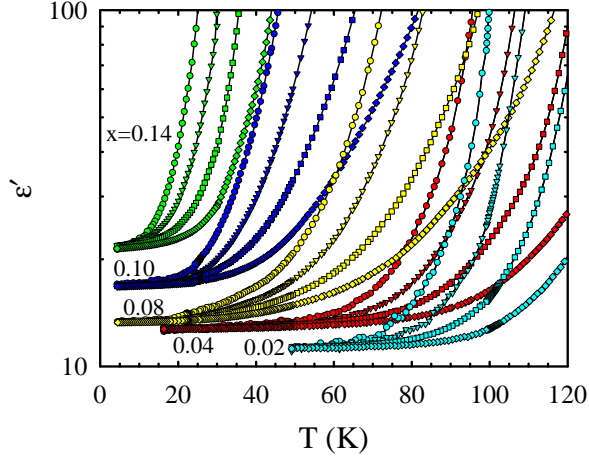


FIG. 1: (Color online)  $\epsilon'$  vs  $T$  for  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$  specimens at frequencies 100 Hz, 1 kHz, 10 kHz, 100 kHz (increasing from left to right for each composition).

specimens used for ac impedance.

### III. RESULTS AND ANALYSIS

Quite generally, the complex dielectric permittivity of a solid,  $\epsilon = \epsilon' - i\epsilon''$ , can be expressed as,  $\epsilon = \epsilon_\infty + \epsilon_l + \epsilon_d$ .  $\epsilon_\infty$  is the high-frequency dielectric constant associated with displacements of ionic charge distributions relative to their nuclei. The lattice contribution,  $\epsilon_l$ , arises from displacements of ions and their charge distributions.  $\epsilon_d$  represents a dipolar contribution, associated in the present materials with charge-carrier hopping as discussed below.  $\epsilon_\infty$  and  $\epsilon_l$  are generally frequency- and temperature-independent at low  $T$ .

Figure 1 shows  $\epsilon'(T)$  at four frequencies for five Ca concentrations in the low- $T$  regime where  $\epsilon'$  becomes frequency and temperature independent. The intrinsic static dielectric constant  $\epsilon_0 \equiv \epsilon'(T \rightarrow 0)$  can be determined directly from the data. The sharp increase of  $\epsilon'(\omega)$  and onset of frequency dispersion with increasing temperature, signatures of dielectric relaxation, are more clearly manifested in the broader temperature range of Fig. 2 (for  $x = 0.08$ ) as steps in  $\epsilon'$  and maxima in the loss factor,  $\tan \delta \equiv \epsilon''/\epsilon'$ .

A significant feature of the relaxation behavior for all specimens is that the temperatures of the maxima in  $\tan \delta$  (denoted  $T_{max}$ ) and inflections in  $\epsilon'(T)$  differ substantially (dashed lines in Fig. 2). This rules out an intrinsic dipole response, for which these features occur at the same temperature.<sup>13,14</sup> Schottky barriers are to be expected at metal-semiconductor contacts with manganites.<sup>12,15</sup> The associated depletion layers behave as a large capacitance in parallel with a resistor, in series with the bulk specimen. Assuming that the contact capacitance is nearly temperature independent, the time constant of the system ( $\tau$ ) is controlled

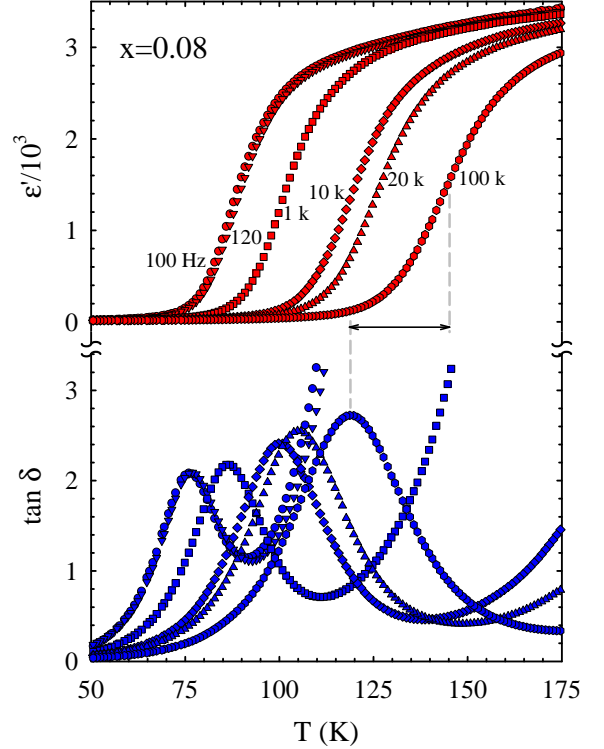


FIG. 2: (Color online)  $\epsilon'$  and loss tangent vs  $T$  at different frequencies for  $x=0.08$ .

by the temperature-dependent bulk resistance of the specimen,<sup>12</sup> with maxima in  $\tan \delta$  occurring for  $\omega\tau \simeq 1$ . Consistent with this picture, Freitas *et al.*<sup>15</sup> have demonstrated for a related manganite compound that large values of  $\epsilon'$  (at  $T \geq 150$  K in Fig. 2) are sensitive to the type of contacts employed (e.g. silver paint, vapor-deposited metals), but that the charge-carrier activation energies derived from the  $\tan \delta$  maxima are contact independent.

Figure 3 shows a semilog plot of  $\omega$  vs  $100/T_{max}$  for several specimens, demonstrating Arrhenius behavior for the relaxation rates,  $\tau^{-1}(T) = \omega_0 \exp(-E_\delta/k_B T)$ . Values of  $E_\delta$  and  $\omega_0$  were determined from the slopes and intercepts, respectively, of linear-least-squares fits (solid lines, Fig. 3) and are listed in Table I.

Figure 4 shows dc resistivity measurements for the same specimens. The low- $T$  data ( $T \leq 160$  K) in Fig. 4 (a) are plotted against  $T^{-1/4}$ , suggesting the variable-range hopping form,<sup>16</sup>  $\rho = \rho_0 \exp[-(T_0/T)^{1/4}]$ . The  $T^{-1/2}$  Efros-Shklovskii<sup>17</sup> hopping form is equally satisfactory over the limited temperature range of the linear least-squares fits (solid lines). High- $T$  resistivity data ( $240 \text{ K} \leq T \leq 440 \text{ K}$ ) in Fig. 4 (b) are shown plotted to emphasize the adiabatic small-polaron form widely established for the paramagnetic phase of these materials,<sup>5,6,7,8</sup>  $\rho/T = A \exp(E_\rho/T/k_B T)$ . Solid lines are linear least-squares fits used to determine  $E_\rho/T$ ; these values and those for  $T_0^{1/4}$  are listed in Table I. The Jahn-Teller (JT) structural transition is clearly evidenced by a vertical displacement of the data for  $x = 0.12$  [arrow in

TABLE I: Nominal Ca and measured  $\text{Mn}^{4+}$  concentrations, dielectric constant, activation energies ( $E_\delta$ ) and prefactors ( $\omega_0$ ) of Arrhenius relaxation rates determined from  $\tan\delta$ , and  $T_0^{1/4}$  and  $E_{\rho/T}$  determined from the dc resistivities for  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$  specimens.

$x$	$p \equiv \text{Mn}^{4+} (\%)$	$\varepsilon_0$	$E_\delta$ (meV)	$\omega_0$ ( $\text{s}^{-1}$ )	$T_0^{1/4}$ ( $\text{K}^{1/4}$ )	$E_{\rho/T}$ (meV)
0.00	4.0	17.6	125	$1.49 \times 10^{11}$	—	—
0.02	5.7	11.3	202	$2.03 \times 10^{13}$	234	231
0.04	7.8	12.7	182	$3.26 \times 10^{12}$	228	232
0.06	9.9	11.7	155	$1.09 \times 10^{12}$	208	233
0.08	11.3	13.8	126	$1.42 \times 10^{11}$	185	233
0.10	12.6	16.3	65.5	$2.58 \times 10^9$	155	233
0.12	14.1	17.8	43.9	$4.42 \times 10^9$	148	220
0.14	17.4	21.4	37.9	$1.05 \times 10^{10}$	134	209
0.15	—	20.9	26.8	$5.21 \times 10^8$	—	—

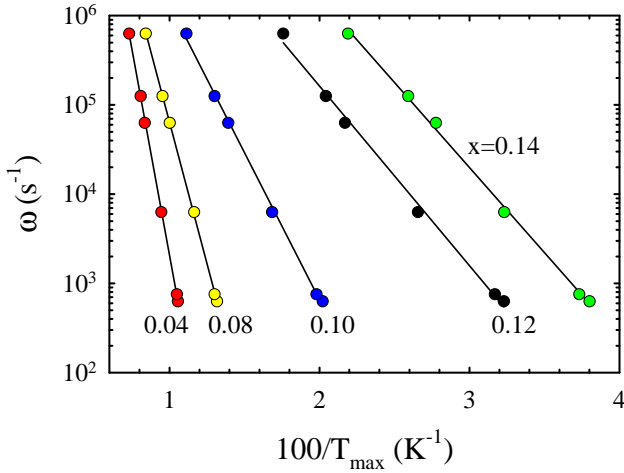


FIG. 3: (Color online)  $\omega$  vs  $100/T_{\max}$  for several Ca concentrations. Solid lines are linear least-squares fits.

Fig. 4 (b)] over a broad temperature interval over which the lattice constants are observed to change.<sup>3</sup> The slopes above and below the transition are the same, in agreement with similar studies of  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ .<sup>8</sup> A transition for the  $x = 0.06$  specimen is also evident, but is not completed at the maximum temperature investigated. The JT transition for the  $x = 0.14$  specimen is expected somewhat below room temperature<sup>3</sup>; the absence of a noticeable feature in  $\rho(T)$  is consistent with the systematic broadening and eventual disappearance of features in structural and magnetic measurements with increased doping near this hole concentration.<sup>3</sup>

#### IV. DISCUSSION

The dependence of  $\varepsilon_0$  on the hole concentration,  $p$ , is shown in Fig 5. For the nominally undoped compound<sup>18</sup>  $\text{LaMnO}_3$ ,  $\varepsilon_0 = 18$ . A smaller value,  $\varepsilon_0 \approx 12$ , is observed for  $p \sim 0.05 - 0.10$ , and an approximately linear

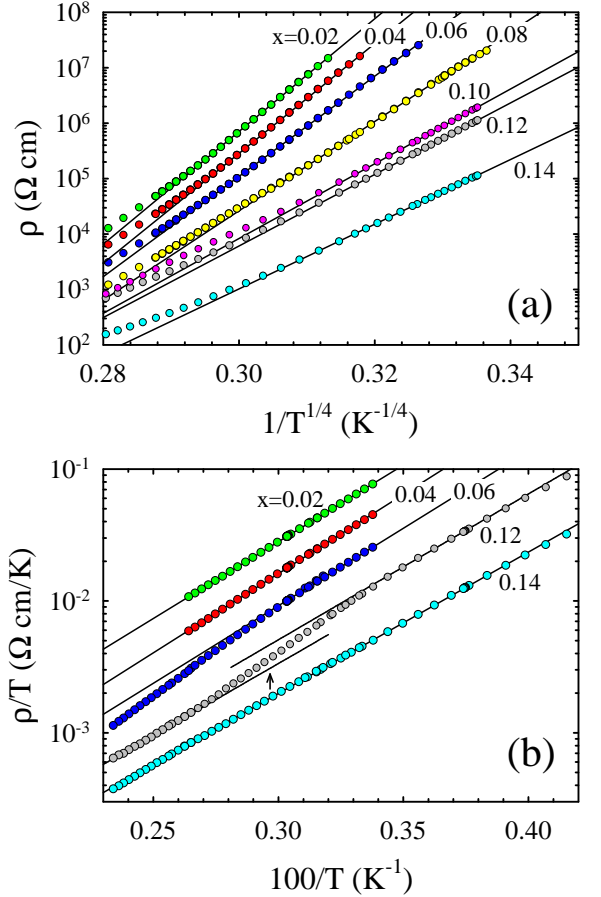


FIG. 4: (Color online) (a)  $\rho$  vs  $1/T^{1/4}$  at low temperatures for  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ , (b) high-temperature data plotted in the adiabatic small-polaron form. Data for  $x = 0.08$  and  $0.10$  are omitted for clarity in (b). Solid lines in both figures are linear least-squares fits.

increase for  $p \geq 0.10$ . Also shown are the magnetic phase boundaries defined by  $T_N$  or  $T_C$  from magnetization data on polycrystals from the same batches as those reported here<sup>9</sup> (squares and right ordinate, Fig. 5) and neutron

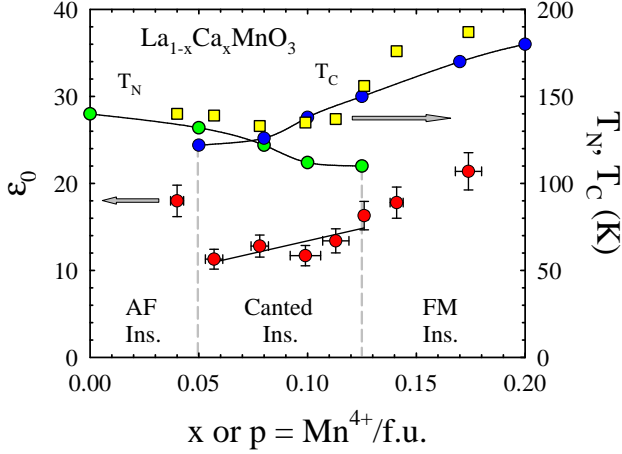


FIG. 5: (Color online)  $\epsilon_0$  vs  $\text{Mn}^{4+}$  concentration from the present study (left ordinate). The solid line is a linear least-squares fit to the data for  $0.057 \leq p \leq 0.126$ . Also shown are data for  $T_N$  and  $T_C$  (right ordinate) determined from magnetization measurements on polycrystalline specimens from the same batch as those used here for dielectric measurements (squares, Ref. 9), and from neutron diffraction on single crystals (circles, Ref. 1). The vertical dashed lines delineate approximate low- $T$  magnetic phase boundaries from Ref. 1.

diffraction studies of single crystals<sup>1</sup> (circles and right ordinate, Fig. 5). The recently clarified structural phase diagram<sup>3</sup> indicates orthorhombic and monoclinic structures for the CAF and FMI regimes, respectively, with a transition occurring in the range  $0.12 \leq p \leq 0.14$ .

Let us first consider the decrease in  $\epsilon_0$  at the lowest hole concentrations. This behavior is contrary to expectations based on the behavior of conventional semiconductors<sup>19</sup> where the dielectric constant of the (undoped) host lattice ( $\epsilon_{0,h}$ ) is enhanced at low temperatures by the presence of electrons or holes bound to donor or acceptor impurities, respectively. Local fields produced by charged defects, La and Mn vacancies, and excess oxygen,<sup>10,11</sup> can influence the polarizability associated with bound holes in the ground state. The observed decrease in  $\epsilon_0$  by  $\sim 30\%$  would require a corresponding decrease in the acceptor polarizability due to differences in the long-range magnetic and/or orbital structure of the A-type AF and CAF states.

The increase of  $\epsilon_0$  for  $p \geq 0.05$  is consistent with a growing contribution from holes bound to acceptors in the present materials (Ca or excess oxygen). An estimate of the polarizability can be found from the solid line in Fig. 5 using the dilute limit of the Castellan-Seitz<sup>20</sup> expression,  $\epsilon_0 - \epsilon_{0,h} = 4\pi N\alpha_0$ , where  $N \equiv p/V_{fu}$  is the acceptor density and  $V_{fu}$  is the volume per formula unit.<sup>9</sup> This yields  $\alpha_0 \simeq 2.8 \times 10^{-22} \text{ cm}^3$  which implies (for hydrogenic impurities) a Bohr radius  $a_H = (2\alpha_0/9\epsilon_{0,h})^{1/3} \simeq 1.7 \text{ \AA}$  (we take  $\epsilon_{0,h} = 12$  from Fig. 5 as representative of the CAF phase). Thus the  $\epsilon_0$  data imply electronic states for the bound holes that are lo-

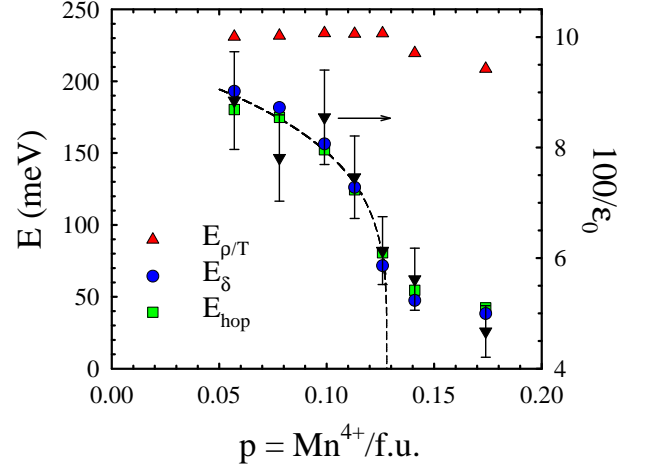


FIG. 6: (Color online) Activation energies (left ordinate) determined from dielectric relaxation ( $E_\delta$ ) and dc resistivities at high- $T$  ( $E_{\rho/T}$ ) and low- $T$  ( $E_{hop}$ ), and inverse dielectric constant (right ordinate) vs  $\text{Mn}^{4+}$  concentration.

calized at individual atomic sites, consistent with general consensus from transport studies near room temperature and above, that doped holes move as small polarons.<sup>5,6,7</sup>

It is instructive to examine and compare the various polaron energies determined from our measurements. As noted above, we expect  $E_\delta$  to represent the low- $T$  charge-carrier hopping energy. Supporting this conclusion we find excellent agreement between  $E_\delta$  and the hopping energy determined from the dc resistivity variable-range hopping fits,<sup>16</sup>  $E_{hop} = 0.25k_B T_0^{1/4} T^{3/4}$ , where  $T$  in this expression was taken as the average  $T_{max}$  for each composition. Figure 6 shows these energies as a function of doping. Also plotted is the high- $T$  polaron activation energy,  $E_{\rho/T}$ , which remains approximately constant at  $\sim 230$  meV up to  $p_c \approx 0.13$ . At higher doping it decreases, a trend quite similar to that reported for  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ .<sup>8</sup> Most striking is the behavior of  $E_{hop}$  which appears to be dropping sharply toward zero at  $p_c$ , and exhibits a clear change in doping dependence for  $p > p_c$ . The dashed curve in Fig. 6 is an empirical power-law fit,  $E_{hop} = 220(1-p/0.128)^{1/4}$ . The inverse dielectric constant, also shown (right ordinate, Fig. 6), appears to follow a very similar behavior.

$E_{hop}(p)$  is reminiscent of the behavior of conventional doped semiconductors<sup>21</sup> near the insulator-metal transition (IMT), with  $p_c$  the critical density. This point of view is encouraged by the observation that  $p_c$  and  $a_H$  are close to satisfying the Mott criterion<sup>22</sup> for an IMT,  $N_c^{1/3} a_H \simeq 0.26 \pm 0.05$ . Experimentally we find  $\approx 0.22$ . Thus the data suggest that the ground-state structural and magnetic transitions<sup>1,3</sup> occurring near  $p_c$  are a consequence of the rapidly growing charge-carrier kinetic energy as  $p \rightarrow p_c$  within the orthorhombic, CAF phase. The change in orbital-ordering scheme in the monoclinic, FMI phase<sup>3</sup> might be viewed as a compromise among

competing magnetic, lattice and Coulomb energies that suppresses the rate of growth in kinetic energy with doping, and “delays” the IMT to higher  $\text{Mn}^{4+}$  concentration. Given this low- $T$  picture of proximity to an IMT, it is natural to hypothesize that the decrease in the high- $T$  small-polaron energy,  $E_{\rho}/T$ , at  $p > p_c$  reflects the cooperative effects of overlapping polarons.

Scaling behavior is to be expected near the IMT, with physical properties controlled by a localization length diverging as  $\xi = \xi_0(1 - p/p_c)^{-\nu}$ , with  $\nu$  a critical exponent. With<sup>16</sup>  $T_0 \propto 1/\xi^3$ , this yields  $T_0^{1/4} \propto (1 - n/n_c)^{3\nu/4}$ , and our empirical fit (dashed curve, Fig. 6) implies  $\nu \simeq 1/3$ . Though smaller than values in the range  $1/2 \leq \nu \leq 1$  that have been reported for doped Si and Ge,<sup>21,23</sup> this estimate of  $\nu$  should be viewed with caution as a lower bound since the scaling theory applies only very close to  $p_c$  where the present data are not sufficiently dense. Furthermore, the inhomogeneous ground state of these materials may alter scaling behavior. This is especially likely near  $p_c$  where both orthorhombic and monoclinic domains may coexist<sup>3</sup> and where the coalescence of ferromagnetic clusters of nanoscopic size embedded in the CAF matrix have been deduced from neutron scattering studies.<sup>1</sup>

In summary, combined dielectric and resistivity measurements reveal new systematics of electronic degrees of freedom in the complex magnetic and structural phase behavior of lightly doped  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ . The doping dependence of the dielectric constant and low- $T$  hopping energies suggest that adding holes within the CAF ground state drives the electronic system toward an insulator-metal transition near  $\text{Mn}^{4+}$  concentration  $\approx 0.13$ . That this transition isn’t realized is evidently a manifestation of competition from magnetic and lattice energies reflected in the emergence of the FMI phase.

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